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(54) Dental ceramic material with low processing temperature

(57) A dental ceramic material for producing repairs of metal ceramic and fully ceramic dental prostheses, that has a processing temperature of  $660 \pm 30^\circ\text{C}$ , has the following composition:

[list:] Gew.% = percent by weight

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- The invention relates to a dental ceramic material for manufacturing and repairing metal ceramic and fully ceramic dental prostheses with a processing temperature of less than 700°C and a thermal expansion coefficient  $\alpha$  of  $13$  to  $14 \cdot 10^{-6} \cdot K^{-1}$  between 20 and 500°C.

Using dental ceramic materials it is possible to produce fully ceramic dental prostheses, to carry out reshaping corrections on metal ceramic and fully ceramic dental prostheses, to repair damaged parts or to face metal dental prostheses with a ceramic layer.

In dental medicine, ceramic layers in the style of an enameling on metal frames (crowns, bridges) have been applied for many years as facing in order to achieve a natural appearance of the dental prosthesis. In this connection, ceramic powders are applied as an aqueous slip onto the metal frame and burned at high temperatures. In this connection, it is important for the combustion temperature (processing temperature) of the ceramic mass to be at least 100°C below the solidifying temperature of the material of the metal frame and for the thermal shock coefficient of the ceramic mass in the 20 to 500°C range to be slightly less than that of the metal material, so that during combustion and cooling, no tears occur in the facing layer.

In the same way as this so-called metal ceramic dental prosthesis, fully ceramic dental prosthesis pieces such as full crowns, partial crowns, insert fillings and facing trays can also be produced in the sintering process with the same ceramic materials on fire-resistant ceramic model materials.

Due to the metal frame materials, dental ceramics of this kind generally need high thermal shock coefficients for facing, which should be from 20 to 500°C at  $13$  to  $14 \cdot 10^{-6} \cdot K^{-1}$ . These ceramics are typically processed at  $950^\circ\text{C} \pm 30^\circ\text{C}$ , which is too high for some dental alloys, however. It is very difficult to substantially decrease the processing temperatures by changing the composition of the dental ceramic, without negatively altering the thermal shock coefficient and the corrosiveness in the process. Biologically questionable elements such as lead oxide must be avoided in the process. Thermal shock coefficients of  $13$  to  $14 \cdot 10^{-6} \cdot K^{-1}$  between 20 and 500°C can be achieved generally only if the dental ceramic masses contain 25 to 30 percent by weight alkali oxides. With this, however, the limit of corrosion resistance of these ceramic is reached in an acid environment such as in the oral cavity below the plaque.

From DE-OS 39 411 460, dental ceramic materials are known for the manufacture, correction and repair of metal ceramic and fully ceramic dental prostheses that contain in addition to SiO<sub>2</sub> as remainder: 5 to 15% Al<sub>2</sub>O<sub>3</sub>, 0.5 to 2.5% B<sub>2</sub>O<sub>3</sub>, 0.5 to 2.5% Sb<sub>2</sub>O<sub>3</sub>, 0.1 to 0.5% CaO, 0.5 to 2.5% BaO, 5 to 10% Na<sub>2</sub>O, 10 to 15% K<sub>2</sub>O, 0.1 to 0.5% Li<sub>2</sub>O and 0.1 to 0.5% F<sub>2</sub>. These may indeed have a thermal shock coefficient between 20 and 500°C of  $13.5 (\pm 1) \cdot 10^{-6} \cdot K^{-1}$ , but their processing temperature of  $730 \pm 30^\circ\text{C}$  is still too high for some dental alloys within facing.

In patent application P 40 31 168.6 not disclosed in advance, ceramic materials for facing of metal dental prostheses are described that have a thermal shock coefficient of  $16$  to  $17.5 \cdot 10^{-6} \cdot K^{-1}$  and a processing temperature of  $770 \pm 70^\circ\text{C}$ . They consist of 60 to 68% SiO<sub>2</sub>, 10 to 15% Al<sub>2</sub>O<sub>3</sub>, 0.7 to 1.5% B<sub>2</sub>O<sub>3</sub>, 0 to 0.5% Sb<sub>2</sub>O<sub>3</sub>, 0 to 0.5% CeO<sub>2</sub>, 0 to 0.5% BaO, 0.1 to 0.5% CaO, 9 to 12% K<sub>2</sub>O, 9 to 11% Na<sub>2</sub>O, 0.8 to 1.4% Li<sub>2</sub>O and 0.2 to 0.4 F<sub>2</sub>.

It was therefore the technical problem of the present invention to develop a dental ceramic material for manufacturing and for repairing metal ceramic and fully ceramic dental prostheses that should have a thermal shock coefficient of  $13$  to  $14 \cdot 10^{-6} \cdot K^{-1}$  between 20 and 500°C and a processing temperature below 700°C. In addition, it should not contain any biologically questionable elements and should be resistant to corrosion in the mouth.

This technical problem is solved according to the invention by a material that consists of 60 to 65 percent by weight SiO<sub>2</sub>, 8.5 to 11 percent by weight Al<sub>2</sub>O<sub>3</sub>, 8 to 12 percent by weight K<sub>2</sub>O, 10.5 to 12 percent by weight Na<sub>2</sub>O, 0.7 to 2 percent by weight CaO, 0.6 to 2 percent by weight BaO, 0.5 to 2.5 percent by weight B<sub>2</sub>O<sub>3</sub>, 0.1 to 0.6 percent by weight Sb<sub>2</sub>O<sub>3</sub>, 0 to 0.5 percent by weight CeO<sub>2</sub>, 1.2 to 3.8 percent by weight TiO<sub>2</sub>, 0.8 to 1.4 percent by weight Li<sub>2</sub>O and 1.2 to 3.8 percent by weight F<sub>2</sub>.

The dental ceramic masses preferably contain 60 to 63 percent by weight SiO<sub>2</sub>, 8.5 to 9.5 percent by weight Al<sub>2</sub>O<sub>3</sub>, 10 to 11.5 percent by weight K<sub>2</sub>O, 10.5 to 11.5 percent by weight Na<sub>2</sub>O, 0.7 to 1.5 percent by weight CaO, 0.6 to 1.2 percent by weight BaO, 0.7 to 1.5 percent by weight B<sub>2</sub>O<sub>3</sub>, 0.2 to 0.4 percent by weight Sb<sub>2</sub>O<sub>3</sub>, 0.1 to 0.4 percent by weight CeO<sub>2</sub>, 1.5 to 3 percent by weight TiO<sub>2</sub>, 0.8 to 1.2 percent by weight Li<sub>2</sub>O and 1.2 to 2.4 percent by weight F<sub>2</sub>.

These dental ceramic materials according to the invention have processing temperatures of  $650 \pm 30^\circ\text{C}$ . In this connection, the glass points are at about  $450^\circ\text{C}$  and the softening points at about  $510^\circ\text{C}$ . They have a very high degree of material homogeneity and a very high degree of transparency (over 70% translucence). Torsion resistance according to DIN 13925 is at  $110 \text{ N} \cdot \text{mm}^{-2}$  and thus far above its minimum requirement of  $50 \text{ N} \cdot \text{mm}^{-2}$ .

The mass loss during the corrosion resistance test according to DIN 13925 (16 hours in 4% acetic acid) is roughly 0.028 percent by weight. In this connection, torsion resistance is surprisingly increased by up to 50%, while it decreases as much as 30% with the known dental ceramics.

The following table shows the composition of a few particularly advantageous materials:

[table: Werkstoff = material]

#### Patent claims

1. Dental ceramic material for manufacturing and repairing metal ceramic and fully ceramic dental prostheses with a processing temperature of less than  $700^\circ\text{C}$  and a thermal expansion coefficient  $\alpha$  of  $13$  to  $4 \cdot 10^{-6} \cdot \text{K}^{-1}$  between  $20$  and  $500^\circ\text{C}$ , characterized by the composition:

60 to 65 percent by weight SiO<sub>2</sub>, 8.5 to 11 percent by weight Al<sub>2</sub>O<sub>3</sub>, 8 to 12 percent by weight K<sub>2</sub>O, 10.5 to 12 percent by weight Na<sub>2</sub>O, 0.7 to 2 percent by weight CaO, 0.6 to 2 percent by weight BaO, 0.5 to 2.5 percent by weight B<sub>2</sub>O<sub>3</sub>, 0.1 to 0.6 percent by weight Sb<sub>2</sub>O<sub>3</sub>, 0 to 0.5 percent by weight CeO<sub>2</sub>, 1.2 to 3.8 percent by weight TiO<sub>2</sub>, 0.8 to 1.4 percent by weight Li<sub>2</sub>O and 1.2 to 3.8 percent by weight F<sub>2</sub>.

2. Dental ceramics material according to claim 1, characterized in that it contains

60 to 63 percent by weight SiO<sub>2</sub>, 8.5 to 9.5 percent by weight Al<sub>2</sub>O<sub>3</sub>, 10 to 11.5 percent by weight K<sub>2</sub>O, 10.5 to 11.5 percent by weight Na<sub>2</sub>O, 0.7 to 1.5 percent by weight CaO, 0.6 to 1.2 percent by weight BaO, 0.7 to 1.5 percent by weight B<sub>2</sub>O<sub>3</sub>, 0.2 to 0.4 percent by weight Sb<sub>2</sub>O<sub>3</sub>, 0.1 to 0.4 percent by weight CeO<sub>2</sub>, 1.5 to 3 percent by weight TiO<sub>2</sub>, 0.8 to 1.2 percent by weight Li<sub>2</sub>O and 1.2 to 2.4 percent by weight F<sub>2</sub>.

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Application number

## EUROPEAN SEARCH REPORT

EP 92 11 9246

| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |   |  |
|--|--|---|--|
| Category   | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No.                       | APPLICATION CLASSIFICATION (Int. Cl. 5)      |
| X, P   | EP-A-O 475 528 (ELEPHANT EDELMETAL B.V.)<br>* Claims 1 - 4; Tables C, G *          | 1 - 2                                       | A61K6/06                                     |
| X, D   | DE-A- 3 911 460 (DUCERA DENTAL GMBH)<br>* the entire document *                    | 1 - 2                                       |  |
| X, P   | EP-A-0 478 937 (DEGUSSA)<br>* the entire document *                                | 1 - 2                                       |  |
| D  | & DE-A- 031 168  |   |  |
| A  | US-A- 6,431,451 (C. MABIE)<br>* column 8, line 32 - line 45; claims *              | 1 - 2                                       |  |
| A  | FR-A- 2 313 912 (JOHNSON & JOHNSON)<br>* column 3, line 10 - line 27; claims *     | 1 - 2                                       |  |
|  |  |   | TECHNICAL FIELDS SEARCHED (Int. Cl. 5)       |
|  |  |   | A61K<br>C03C                                 |
| This search report was drawn up for all claims   |  |   |  |
| Place of search<br>THE HAGUE   |  | Search completion date<br>FEBRUARY 23, 1993 | Authorized officer<br>G. COUSINS - VAN STEEN |
| CATEGORIES OF CITED DOCUMENTS  |  |   |  |
| <p>X: particularly relevant by itself</p> <p>Y: particularly relevant in combination with another document of the same category</p> <p>A: technological background</p> <p>O: oral disclosure</p> <p>P: document published prior to the filing date but later than the priority date claimed</p> <p>T: theory or principle underlying the invention</p> <p>E: earlier document but published on or after the filing date</p> <p>D: cited in the application</p> <p>L: cited for other reasons</p> <p>&amp;: document member of the same patent family</p> |  |   |  |